

Molecular Simulations of Water Adsorption in Non-Activated Graphitic Micropores: the Hysteresis Phase Diagram

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Because of a delicate equilibrium between strong water-water and weak water-carbon interactions, adsorption isotherms for water in carbon-based materials are often characterized by negligible fluid uptake at low pressures, by pore filling according to the capillary-condensation mechanism, and by large adsorption/desorption hysteresis loops. The size of the hysteresis loops decreases with increasing temperature.

By simulating adsorption isotherms at various temperatures in the range 298 to 498 K, and by recording at each temperature the pressure-density conditions that inscribe the hysteresis loops, we constructed the hysteresis phase diagram for SPC/E water confined in 0.8, 1.0 and 1.6 nm-wide carbon slit pores. By doing so, we obtained the ‘hysteresis critical temperature’, which is the temperature at which the hysteresis loop disappears for each pore considered. Our results show that by reducing the pore width to less than a nanometer the hysteresis critical temperature is approximately 150 K lower than the critical temperature for bulk SPC/E model water (i.e. about 640 K).

The simulation results here reported are confirmed by experimental adsorption isotherms measured by a gravimetric technique for water in various carbon monoliths. The monodisperse pores of the materials considered are of comparable size to those simulated. Experimental temperatures considered are in the range 373 to 450 K.